

## SYNTHESIS OF ZEOLITE ITQ-16 IN AN ALKALINE MEDIUM

### RELATED APPLICATIONS

[0001] The present application is a Continuation of co-pending PCT Application No. PCT/ES02/00057, filed February 8, 2002 which in turn, claims priority from Spanish Application Serial No. 200100385, filed on February 9, 2001. Applicants claim the benefits of 35 U.S.C. §120 as to the PCT application and priority under 35 U.S.C. §119 as to said Spanish application, and the entire disclosures of both applications are incorporated herein by reference in their entireties.

### TECHNICAL FIELD

[0002] Microporous crystalline materials

### BACKGROUND

[0003] Zeolite Beta is a microporous material with channels formed by 12 member rings, that has a characteristic diffraction pattern (Pérez-Pariente, J., Martens, J.A., Jacobs, P.A., Applied Catalysis, 31, (1987) 35).

[0004] This zeolite is formed by intergrowth of different polymorphs related to each other, just as it has been described in literature (J.M. Newsam, M.M.J. Treacy, W.T. Koetsier, C.B. de Gruyter, Proc. R. Soc. London A. 420 (1988)375). Of all the polymorphs described, it seems that polymorphs A and B are the ones that basically form intergrowth called zeolite Beta (Zeolites, 5/6, (1996), 641) while the polymorph C is found in a smaller proportion in said intergrowth.

[0005] Hence, it should be possible to synthesize new materials with proportions different from those of the different polymorphs A, B and C that would lead to structures with an X-ray diffractogram different from that of zeolite Beta just as it is defined in accordance with its X-ray diffractogram, and different from that of the pure polymorph C.

### Description of the Invention

[0006] The present invention refers to a process for synthesis in an  $\text{OH}^-$  medium and in the absence of fluorides, of a new family of zeolitic materials that fit in the name ITQ-16, and to its catalytic uses.

[0007] Zeolite ITQ-16 is related to zeolite Beta, but has a different X-ray diffractogram which is attributed to the presence of a proportion of the different polymorphs different from the one that has been found in zeolite Beta. Hence, zeolite ITQ-16 could be comprised, aside from polymorphs A and B characteristic of zeolite Beta, of another polymorph that could correspond to polymorph C proposed by Newsam et al. (J.M. Newsam, M.M.J. Treacy, W.T. Koetsier, C.B. de Gruyter. Proc. R. Soc. London A, 420 (1988) 375.) Therefore, the presence of this other polymorph gives the material ITQ-16 a characteristic X-ray diffraction pattern different from the one of zeolite Beta.

[0008] The X-ray diffraction pattern of the material ITQ-16, just as it is synthesized, has been obtained in a Philips PW 1830 diffractometer with a PW 1710 controller and using  $\text{Cu K}\alpha$  radiation. The diffractogram obtained by means of the powder method and using a variable divergence crack is shown in Table I and is characterized by the following  $2\theta$  angle (degrees) and relative

intensities ( $I/I_0$ ),  $I_0$  being the intensity of the most intense peak to which a value of 100 is given. Relative intensities have been expressed in the following terms w = weak intensity (between 0 and 20%); a = average intensity (between 20 and 40%); s = strong intensity (between 40 and 60%) and vs = very strong intensity (between 60 and 100%).

[0009]

Table I

2 $\theta$ (degrees)	Intensity
6.91	w
7.68	w
9.60	a
15.16	w
19.35	w
21.03	w
21.39	w
22.00	vs
23.19	w
25.03	w
26.04	w
27.08	a
27.89	w
29.32	w
30.51	w
32.83	w
34.46	w
35.27	w
35.93	w
39.22	w

[0010] The variation in the measurements of the 2 $\theta$  angle due to the instrumental error is estimated at  $\pm 0.05$  degrees.

**[0011]** The positions, widths and relative intensities of the diffraction peaks can be modified according to the chemical composition of the material (type of structure directing agent, Si/Ge ratio, presence of other trivalent and/or tetravalent heteroatoms (one or several) in the lattice, aside from silicon and/or germanium, such as for example: aluminum, boron, titanium, vanadium, etc.), as well as the degree of hydratio and crystal size. In particular, the pattern represented in table I refers to materials whose lattice is comprised exclusively of silicon and germanium oxide, with a Si/Ge ratio = 5 and synthesized using the benzyl-DABCO (BD<sup>+</sup>) cation, as structure directing agent.

**[0012]** Table 2 shows the values of the 2θ angle and relative intensities (I/I<sub>0</sub>) of the X-ray diffractogram reflections of powder of the prior sample of ITQ-16 after being roasted at 580°C in order to eliminate the organic compounds occluded inside the zeolite, wherein w, a, s and vs have the same meanings as in table I.

**[0013]**

**Table II**

6.87	s
7.64	a
9.60	s
13.32	w
13.88	w
15.39	w
19.25	w
19.97	w
21.15	a
22.10	vs
23.24	w
25.01	w
26.81	a
27.98	w

29.25	w
30.28	w
31.79	w
32.88	w
34.36	w
35.16	w
35.97	w
39.25	w

**[0014]** The X-ray diffraction pattern of zeolite ITQ-16 mainly differs, with respect to zeolite Beta, in that at low angles it has, aside from a wide peak with a value of  $2\theta$  around  $7.6^\circ$ , two peaks at  $2\theta$  angles of  $6.9^\circ$  and  $9.6^\circ$ , that in general show a smaller width at an average height than the peak at  $7.6^\circ$ .

**[0015]** The relative intensity of these peaks varies since the proportion of the polymorphs A, B and C in the ITQ-16 zeolite structure, varies, the limits being the pure polymorph C, proposed by Newsan, and zeolite Beta (Pérez-Pariente, J., Martens, J.A., Jacobs, P.A., Applied Catalysis, 31 (1987) 35) US patent Re28341).

**[0016]** Therefore, this specification describes the process of synthesis of a family of materials that has zeolite Beta and another polymorph that could be polymorph C as the extreme and outside limits. Contrary to what happens in zeolite ITQ-16, the peaks at angles  $6.9^\circ$ ,  $7.6^\circ$  and  $9.6^\circ$  are not found simultaneously in zeolite Beta and in the possible polymorph C.

**[0017]** The present invention refers to a new process of synthesis of a material named ITQ-16, characterized by means of synthesis with an initial pH between 14 and 9 and preferably between 13 and 10 and the use of hydroxide anions as a mineralizing agent, and without introducing

fluoride anions as mineralizing agents, and the presence of organic compounds as structure directing agents.

**[0018]** Said organic compounds can be cations of the tetraalkylammonium type with a general formula  $(R_1R_2R_3R_4N)^+$  wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  can be alkyl or aromatic chains with 1 to 16 carbon atoms, that may or may not form cycles on the nitrogen atom. Besides, the use of organic polycations with a general formula of  $R_mN_x((CH_2)_n)_p$  wherein  $x$  may have values between 2 and 12, is also described.  $n$  refers to the number of carbon atoms that form some of the alkyl chains bridge between two contiguous nitrogen atoms and may vary between 1 and 6;  $p$  refers to the number of alkyl chains a bridge existing between nitrogen atoms and it can vary between 2 and 24, and  $R$  refers to alkyl or aryl groups bonded to a single nitrogen (N) atom containing between 1 and 12 carbon atoms and  $m$  has a value that can vary between 0 and 36.

**[0019]** The preparation process of the present invention is based on heating at temperatures between 80°C and 250°C and preferably between 130°C and 175°C a reaction mixture that contains a Si source, among which amorphous silica, colloidal silica, silica gel, tetraalkylorthosilicate, sodium silicate and a germanium source such as for example germanium oxides, halides or alkoxides are preferred. The synthesis mixture contains one or more of the following organic cations in their hydroxide form as a structure directing agent, without this being restrictive:  $TEA^+$ ,  $BD^+$ ,  $BQ^+$ ,  $m\text{-XydQ}^{2+}$ ,  $M_4BD^{2+}$ ,  $C_yHMP^+$   $MCyHMP^+$ . Alternatively, it is possible to use the organic cation in the form of a salt (for example, a halide, preferably chloride or bromide) and adding a source of alkaline or alkaline earth ions, preferably in the form of a hydroxide.

**[0020]** Optionally, trivalent cations such as for example Al, B, Ga, Fe or Cr, and/or tetravalent cations such as Ti, V or Sn can be introduced in the synthesis gel.

**[0021]** On occasions it may also be convenient to add at some point of the preparatio process a crystalline material, preferably a zeolitic material and more preferably ITQ-16 crystals (between 0.01 and 25% by weight with respect to all the inorganic oxides together, preferably between 0.05% and 10% by weight) as crystallization (seeding) promoters.

**[0022]** In the particular case of using the BD cation as a structure directing agent, the composition of the synthesis mixture is characterized by the following ranges of molar ratios:

$BD/(SiO_2+GeO_2)$  = between 3 and 0.01 and preferably between 1 and 0.03.

$H_2O/(SiO_2+GeO_2)$  = between 1000 and 0.5, and preferably between 100 and 2.

$GeO_2/(SiO_2+GeO_2)$ , defined as  $g$ ; = between 0.8 and 0.005, and preferably between 0.5 and 0.032, and more preferably between 0.333 and 0.0625.

$(Si+Ge)/X$  = between 5 and  $\infty$  and preferably higher than 15, and more preferably higher than 20.

$SiO_2+GeO_2/TO_2$  = between 10 and  $\infty$ , and preferably between 1 and 0, and more preferably between 0.5 and 0.

$M^{n+}/SiO_2+GeO_2$  = between 2 and 0, preferably between 1 and 0, and more preferably between 0.5 and 0.

wherein X represents an element in its trivalent oxidation state such as Al, B, Fe, Ga or Cr; T is an element in its tetravalent oxidation state such as Ti, Sn or V and M is an alkaline or alkaline earth cation such as  $Na^+$ ,  $Ba^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ , etc.

**[0023]** Once crystallization is complete, the solids are separated from the mother liquors by filtration or centrifugation. A highly crystalline solid that contains occluded organic material is obtained as a result.

**[0024]** The solid product obtained has a characteristic diffraction pattern (CuK $\alpha$  radiation) just as it is presented in table I, and that has a certain similarity with the one of zeolite Beta (US patent Re28341) at a high angle  $2\theta > 20^\circ$ , wherein  $\theta$  is the Bragg angle and has little similarity at low angles.

**[0025]** The occluded organic material is eliminated by vacuum roasting, air, N<sub>2</sub> or another inert gas, at a temperature higher than 450°C, and preferably at a temperature higher than 500°C and lower than 900°C. The X-ray diffraction pattern of the roasted material is shown in table II.

**[0026]** Hence, roasted zeolite ITQ-16 has a diffraction peak around 7.6°, characterized by a width at medium height of around 1° and characteristic of zeolite Beta (Newsam et al., Proc. R. Soc. London A, 1988, 420, 375) with a certain intergrowth of polymorphs A and B, but it also has two peaks at 6.9° and 9.6° corresponding to the presence of another polymorph that could be the polymorph C. Hence, zeolite ITQ-16 has a degree of intergrowth different from that of zeolite Beta.

**[0027]** The material in its roasted form has the following empirical formula:



wherein T may be one or several elements with a +4 oxidation state different from Ge and Si such as for example Ti, V, Sn; X may be one or several elements with



a +3 oxidation state such as for example Al, Ga, B, Cr, Fe and M may be  $H^+$  or one or several +n charge compensation inorganic cations such as for example  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$   $Mg^{2+}$ , etc.

**[0028]** The value of  $g$  should be between 0.8 and 0.005, and preferably between 0.5 and 0.032, and more preferably between 0.333 and 0.0625. The  $SiO_2+GeO_2/TO_2$  is between 10 and  $\infty$ , preferably higher than 20. In the event that zeolite ITQ-16 is to be synthesized with trivalent cations, X, such as for example Al, the Si+Ge/Al ratio is comprised between 5 and  $\infty$ , and preferably higher than 15, and more preferably higher than 20.

**[0029]** The following uses for the zeolite ITQ-16 synthesized in the present specification are described in the present specification:

- as components of catalysts in a cracking process, of catalytic cracking of hydrocarbides, and in general of organic compounds in a hydrocracking process, an olefin hydroisomerization process, a light paraffin isomerization process, a dewaxing or isodewaxing of paraffin process,
- as a component or additive of light paraffin isomerization catalysts,
- as components of catalysts in a hydrocracking process selected among gentle hydrocracking of hydrocarbides and gentle hydrocracking of functionalized hydrocarbides,
- as catalysts in an alkylation process selected from among alkylation of olefins with isoparaffins, alkylation of isoparaffins with olefins and alkylation of aromatics or aromatic substituted with olefins or alcohols, in particular in a process of alkylation of benzene with propylene,

- as catalysts in an Oppenauer oxidation process, or a Meerwein-Ponndorf-Verley type reduction process or
- as catalysts in acylation reactions of aromatic compounds substituted by using acids, acid or anhydride chlorides of organic acids as acylating agents.

**[0030]** The materials prepared according to the process of the invention that contain Ti, V or Sn can be used in selective oxidation processes of organic compounds using  $H_2O_2$  or organic peroxides or hydroperoxides as oxidizing agents.

**[0031]** The materials prepared according to the process of the invention that contain Sn, may be used in Baeyer-Villiger type oxidation processes.

**[0032]** The materials prepared according to the process of the invention may also be used as components of catalysts in order to eliminate organic vapors (OVC).

**[0033]** In the case of ITQ-16 containing Ti, use thereof as a catalyst of olefin epoxydation, alkane oxidation, alcohol oxidation and oxidation of thioethers to sulfoxides and sulfanes using organic or inorganic hydroperoxide, such as for example  $H_2O_2$ , tetrabutylhydroperoxide, cumene hydroperoxide, as oxidating agents, is claimed.

**[0034]** In the event that Sn is contained, use thereof is claimed as oxidation catalysts in Bayer-Williger reactions using  $H_2O_2$  as the oxidizing agents. Finally, use thereof in amoxymation of cyclohexanone to cyclohexanone oxime with  $NH_3$  and  $H_2O$ , is claimed.

### BRIEF DESCRIPTION OF THE FIGURES

**[0035]** Figure 1 shows a characteristic diffraction pattern of zeolite Beta.

**[0036]** Figure 2 shows a diffractogram of the polymorph C of zeolite Beta calculated from the structure proposed in *Proc. R. Soc. London A*, 420 (1988) 375.

**[0037]** Figure 3 shows an X-ray diffractogram of zeolite ITQ-16 without roasting, whose lattice is comprised of materials that only contain silicon and germanium oxide, that corresponds to the data contained in Table I.

**[0038]** Figure 4 shows various organic cations that may be used as a structure directing agent.

**[0039]** Figure 5 shows the diffraction pattern of roasted zeolite ITQ-15, that corresponds to the data given in Table II.

**[0040]** Figure 6 shows the characteristic diffraction pattern of zeolite ITQ-16 prepared according to example 2.

**[0041]** Figure 7 shows the characteristic diffraction pattern of zeolite ITQ-16 prepared according to example 3.

**[0042]** Figure 8 shows the characteristic diffraction pattern of zeolite ITQ-16 prepared according to example 4.

**[0043]** Figure 9 shows the characteristic diffraction pattern of zeolite ITQ-16 prepared according to example 5.

## EXAMPLES

### **[0044] Example 1**

7.21 g of tetraethylorthosilicate (TEOS) are hydrolyzed in 20.22 g of an aqueous solution of BD ( $9.27 \cdot 10^{-4}$  moles of BD(OH)/g). Then 0.653 g. of  $\text{GeO}_2$  are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS and 12.3 g. of water. The resulting mixture is heated in autoclaves coated inside with PFTE at  $150^\circ\text{C}$ . After heating the mixture for 4.5 days same is filtered and 22 g. of zeolite ITQ-16 per 100 g of synthesis gel are obtained.

The X-ray diffraction pattern is presented in figure 3.

### **[0045] Example 2**

7.21 g of tetraethylorthosilicate (TEOS) are hydrolyzed in 20.22 g of an aqueous solution of BD ( $9.27 \cdot 10^{-4}$  moles of BD(OH)/g). Then 0.653 g. of  $\text{GeO}_2$  and 0.077 g Se aluminum isoperoxide are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS and 12.3 g. of water. The resulting mixture is heated in autoclaves coated inside with PFTE at  $150^\circ$ . After heating the mixture for 7 days same is filtered and 18 g. of zeolite ITQ-16 per 100 g of synthesis gel are obtained.

The X-ray diffraction pattern is presented in figure 6.

**[0046] Example 3**

9.37 g of tetraethylorthosilicate (TEOS) are hydrolyzed in 20.71 g of an aqueous solution of BD ( $2.0 \cdot 10^{-3}$  moles of BD(OH)/g). Then 0.313 g. of  $\text{GeO}_2$  are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS and 10.34 g. of water. The resulting mixture is heated in autoclaves coated inside with PFTE at  $135^\circ$ . After heating the mixture for 6 days same is filtered and 24 g. of zeolite ITQ-16 per 100 g of synthesis gel are obtained.

The X-ray diffraction pattern is presented in figure 7.

**[0047] Example 4**

5.21 g of tetraethylorthosilicate (TEOS) are hydrolyzed in 20.22 g of an aqueous dissolution of BD ( $9.27 \cdot 10^{-4}$  moles of BD(OH)/g). Then 1.307 g. of  $\text{GeO}_2$  are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS and 12.5 g. of water. The resulting mixture is heated in 5.21 of tetraethylorthosilicate (TEOS), hydrolyzed in 20.2 g of an aqueous solution of BD ( $9.27 \cdot 10^{-4}$  moles of BD(OH)/g). Then 1.307 g of  $\text{GeO}_2$  are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS, in autoclaves coated inside with PFTE at  $150^\circ\text{C}$ . After heating the mixture for 1 day same is filtered and 13 g. of zeolite ITQ-16 per 100 g of synthesis gel are obtained.

The X-ray diffraction pattern is presented in figure 8.

**[0048] Example 5**

5.21 g of tetraethylorthosilicate (TEOS) are hydrolyzed in 14.9 g of an aqueous solution of m-XydQ ( $9.37 \cdot 10^{-3}$  m m-XydQ(OH)<sub>2</sub>/g). Then 1.307 g. of GeO<sub>2</sub> are added. The mixture is left stirring and evaporating the ethanol formed in hydrolysis of TEOS and 2.8 g. of water. The resulting mixture is heated in autoclaves coated inside with PFTE at 150°. After heating the mixture for 7 days same is filtered and 13 g. of zeolite ITQ-16 per 100 g of synthesis gel are obtained.

The X-ray diffraction pattern is presented in figure 9.